Results in Physics 5 (2015) 105–110

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Raman, morphology and electrical behavior of nanocomposites based on PEO/PVDF with multi-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 3 April 2015
Accepted 22 April 2015
Available online 2 May 2015

Keywords:
MWCNTs
Nanocomposites
Raman spectroscopy
TEM
AC conductivity

ABSTRACT

In this work, FT-IR, Raman, TEM spectroscopy and AC conductivity were used to study and characterize of PEO/PVDF blend incorporated with low content of multi-walled carbon nanotubes (MWCNTs). Main characteristics of IR and Raman bands for the two polymers and MWCNTs were observed. The shift of G, D and G″ bands of MWCNTs occurred. All results showed that MWNTs-COOH were covalently linked with the blend through OH and C–C bonds. TEM images illustrated that MWNTs were well dispersed into polymeric matrices and wrapped with PEO/PVDF chains. The temperature dependent conductivity measurements of nanocomposites were studied. The addition of MWCNTs increases and enhances the conductivity attributed to charge carrier build up and increases in segmental mobility of polymeric chains. Molecules in the loaded samples begin to bridge the gap which separates them by lowering potential barriers and the localized state between them. Values of both ε' and ε'' are high at lower frequency and decrease with an increase of frequencies due to polarization effects.

1. Introduction

Carbon nanotubes (CNTs) incorporated into the polymeric matrices is attractive method to combine the optical, electrical and mechanical properties of individual CNTs with the advantages of the polymer [1–4]. These unique properties of CNTs make an ideal reinforcing agent in a number of applications. The properties depend on the structural perfection and the ratio of CNTs. Single walled carbon nanotubes (SWCNTs) consist of a single sheet of graphene wrapped into cylindrical tubes with diameters around 2 nm with some micrometers in length. Multi-walled carbon nanotubes (MWCNTs) consist of sets of SWCNTs having larger diameters [5–7]. Until now, low compatibility and limitation of dispersion of CNTs polymeric matrices occur but the interaction between CNTs and the polymer remains weak. CNTs form long bundles due to stabilization by π–π electron interactions and high surface energy. Lowering costs of CNTs (especially MWCNTs) with an increase in demand and production for a huge polymer-CNT nanocomposites market give activity to more research [8–10].

Depending on preparation conditions, PVDF is presented in many types of molecular and crystal structures. The main forms of PVDF have distinct molecular conformations. The unit cell of form I (β-phase) contains polymer chains with an all trans structure (TTT), form II (α-phase) presents trans-Gauche sequences (TGTGTG) and form III (γ-phase) presents trans bonds separated by a Gauche bond in sequences (TGTḠ). Infrared and Raman analyses are used to distinguish the different forms of PVDF [11–13].

Spectroscopic and electrical studies are good techniques to investigate and characterize nanocomposites to evaluate properties relevant to performance. In these techniques, we study the host polymeric matrices as individual polymers and how their properties are affected by dispersion of MWCNTs in polymeric matrices [14].

PEO and PVDF have been studied due to their appealing properties such as high dielectric constant ($\varepsilon \approx 8.4$) and strongly electro withdrawing functional groups (C–F) [15]. The order of the ionic conductivity of pure PEO is around 10^{-7} to 10^{-6} S cm^{-1} at room temperature [16] and the order of conductivity is not suitable for practical applications. The order of ionic conductivity was improved with the addition of MWCNTs to the pure PEO/PVDF blend.

The blend between the polymers provides easy preparation and control experimentally of the physical properties within the miscibility region in the blend. The exhibits properties are superior for the properties of the individual component of the blend [17,18]. Recently, many efforts have been devoted to increase the ionic

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http://dx.doi.org/10.1016/j.rinp.2015.04.005
2211-3797/

conductivity of blend-based polymer electrolytes such as PVDF/PEO. Fan et al. [19] reported that the blend of PEO and PVDF could hinder the crystallinity of PEO and achieve a good combination of high ionic conductivity and good mechanical strength.

On the other hand, nanosized MWCNTs, due to its large surface area, prevents local PEO chain re-organization, which results in "locking in" at ambient temperatures, a high degree of disorder characteristic of the amorphous phase, which in turn favors high ionic transport. Addition of the polymer blend was found to increase room temperature conductivities by about 2–3 orders of magnitude, resulting in increased carbon ion transference numbers and improved electrical properties [20]. The high surface to volume ratio of MWCNTs facilitates the attainment of desired macroscopic functionality at lower fractions.

Dispersion of multi-walled carbon nanotubes (MWCNTs) nanotubes in polymeric matrices is one of the most critical issues in MWCNTs/polymer nanocomposites. In this paper we discuss the considerable improvement in the dispersion of MWNTs in PEO/PVDF matrix. This paper reports some investigations and characterization carried out by FT-IR, Raman and TEM spectroscopy on PEO/PVDF blend, MWCNTs and on PEO/PEVDF incorporated with different contents of MWCNTs nanocomposites.

2. Experimental

2.1. Materials

Polyethylene oxide (PEO) of molecular weight 900,000 supplied from ACROS (New Jersey, USA) and polyvinylidene fluoride (PVDF) with *Mw* = 180,000 supplied from Aldrich, USA. Purified multi-walled carbon nanotubes (MWCNTs) with COOH functional groups (NTX10) were obtained from Nanothinx, Greece. MWCNTs-COOH have a diameter of 8–14 nm, length ⩾ 5 μm and a purity of 88%.

2.2. Preparation of nanocomposites films

Firstly, PEO and PVDF were dried in a vacuum oven at 50 °C about 1 h to remove moisture content. Some amount of both PEO (20%) and PVDF (80%) was dissolved in dimethyl sulfoxide (DMSO) as a solvent at 60 °C with stirring. Polymer solutions after complete dissolution and at suitable viscosity were obtained. The obtained solution of the blend was then cooled to room temperature for about 3 h to remove any bubbles. MWCNTs-COOH were added separately to 10 ml of DMSO on a beaker. The beaker was immersed, to give suspension; in on the ultrasonic (Eltrosonic type-07) about 40 min. PVDF/PEO nanocomposites containing MWCNTs were prepared using casting method by the following procedure. Suspension solutions of MWCNTs-COOH were prepared using continuous stirring under ultrasonic. The MWCNTs solution was added dropwise to blend solution with continuous stirring. The concentration of MWCNTs namely, 0.05 and 0.1 wt.%. After careful mixing of blend solution with MWCNTs dispersions followed by casting of PVDF/PEO/MWCNTs nanocomposite films were obtained by peeling off from PET Petri dishes. The nanocomposite solution was put in an oven at 60 °C to evaporate the solvent for about 48 h. The prepared samples were kept in a vacuum desiccator before measurement. The thickness of the resulting film was about 20 μm.

2.3. Measurement techniques

FT-IR spectra of the prepared samples were carried out using the single beam Fourier transform-infrared spectrometer (FT-IR-430, JASCO, Japan) in the spectral range of 4000–400 cm^{-1}. Raman spectra were recorded in the backscattering geometry on a Labram HR (Jobin–Yvon, Horiba Group, France) microspectrometer using a 50 mW power laser at 532 nm. Transmission electron microscope (TEM), (JEOL-JEM-1011, Japan) was carried out to study the diameter, shape, length and distribution of the nanoparticles within the polymeric matrix during the preparation process. Samples for TEM were prepared by dropping the ethanol suspension of MWCNTs onto a copper grid which was left to dry in air about 30 min. AC measurements were obtained using LCR meter models (Model Hioki 3531Z Hitester). The film with 30 μm was placed in a holder specially designed to minimize stray capacitance. The range of frequency was from 42 Hz to 10 MHz. The measurements give the resistance (R), capacitance (C_p) and dissipation factor (D) of the samples in the temperature range from 303 K to 433 K.

The total conductivity (σ) was calculated from the relation [21]:

$$\sigma(\omega) = \frac{d}{RA} = \sigma_{AC} + \sigma_{DC} \quad (1)$$

where d (cm) is the thickness of the sample, R is the resistance, A is the cross section area, σ_{AC} is the AC electrical conductivity and σ_{DC} is the DC conductivity.

The real part of dielectric constant ε' was calculated from [22]:

$$\varepsilon' = \frac{C_p \cdot d}{\epsilon_0 \cdot A} = \frac{\varepsilon''}{\tan\delta} \quad (2)$$

where ε_0 is the permittivity of free space (8.9×10^{-12} F m^{-1}) and ε'' is the dielectric loss.

3. Results and discussion

3.1. FT-IR and Raman studies

Fig. 1 shows FT-IR absorption spectra for pristine PEO, PVDF and PEO/PVDF blend. Most of characteristic IR bands of both polymers are observed below 2000 cm^{-1}in the spectra. The strong band of PEO appears to be C–O–C stretching vibration mode at 1094 cm^{-1}. The CH_2 scissoring at 1456 cm^{-1}, CH_2 bending at 1341 cm^{-1}, C–O–C binding at 1276 cm^{-1}, C–O binding at 1240 cm^{-1}, out of plane at 925 cm^{-1}. However, the band feature above 2000 cm^{-1} is intense and composition sensitive. They are the C–H symmetric stretching at 2880 cm^{-1} [23].

The main bands of pristine PVDF are ascribed as: The IR bands at 552 and 796 cm^{-1} corresponded to the α-phase of PVDF while the IR bands at 488 and 839 and 876 cm^{-1} are attributed to the β-phase of PVDF. The bands at 552 and 840 cm^{-1} are assigned to

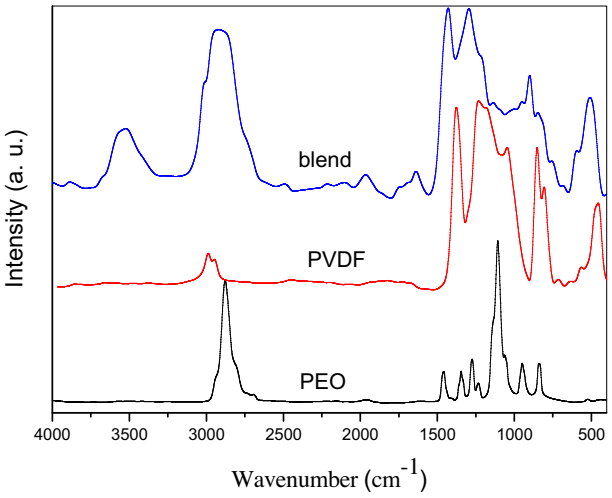

Fig. 1. FT-IR spectra of pure PEO, pure PVDF and PEO/PVDF blend.

CF_2 bending and at 796 $cm^{-1}$is assigned to CF_2 skeletal vibrational mode. The bands at 796 and 839 cm^{-1} are attributed to CH_2 rocking. Splitting band around 1180 cm^{-1}resulted from the stretching vibration of CF [24–27].

The spectrum of PEO/PVDF blend shows some shifts in the band position, band intensities and disappearance of other bands. These may be due to a good miscibility and interaction between PEO and PVDF. In general, the blend comprising the two compounds shows spectrum characteristics of both, but the vibrational bands characterizing each polymer are predominate. The PEO vibration bands at 194 $cm^{-1}$and 925 cm^{-1} disappeared. This is attributed to specific interaction between fluorine in PVDF and carbon connected to oxygen of PEO.

The FT-IR spectra of PEO/PVDF blend doped with 0.05 wt.% and 0.1 wt.% of MWCNTS are shown in Fig. 2. A new band is observed at 840 cm^{-1}corresponding to C–C–C group of MWCNTs. The broadness in the bandsat 3500 and 840 cm^{-1} are increases attributed to the function group (OH) which was added during functionalization (adding COOH group) to MWCNTs. The strong band at 1685 cm^{-1}could be attributed to the presence of stretching vibrations of (C═O) in the carbonyl group (COOH) supporting carboxyl functionalization on the surface of MWCNTs. The band at 840 $cm^{-1}$for the β-PVDF crystal phase increased with an increase of the amount of MWCNTs due to the role of MWCNT as nuclei for the rapid crystallization through increasing the crystalline rate.

3.2. Raman spectroscopy

Fig. 3 shows Raman spectra for pristine PEO, PVDF and MWCNTs. The main characteristic bands of raw MWCNTs are observed at 1590 cm^{-1} (G-band) and 1430 cm^{-1} (D-band). The G-band is an intrinsic feature of carbon nanotubes that is related to vibrations in all sp carbon materials. The most important aspect of the G-band is the characteristic Raman line shape. The two main graphite bands are present in the Raman spectrum of MWCNTs bundles: the band at 1580 cm^{-1} (G band) assigned to the in-plane vibration of the C–C bond. The G band is a tangential shear mode of carbon atoms that corresponds to the stretching mode in the graphite plane. The band at 1341 cm^{-1} (D band) is activated by the presence of disorder in carbon systems. The Raman spectrum also exhibits a band at 2682 cm^{-1} called the G'' band attributed to the overtone of the D band. Some Raman bands are present located at 2888 and 2980 cm^{-1} called the G′-band [28–30]. The frequency of these bands is close to twice that of the D band.

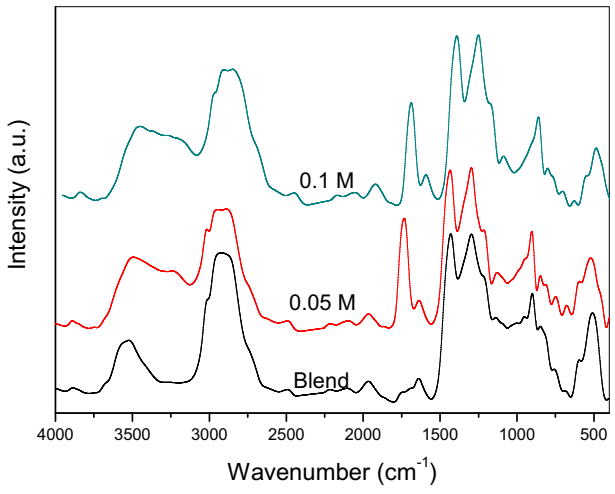

Fig. 2. FT-IR spectra of PEO/PVDF blend and the blend doped with 0.05 and 0.1 wt.% of MWCNTs.

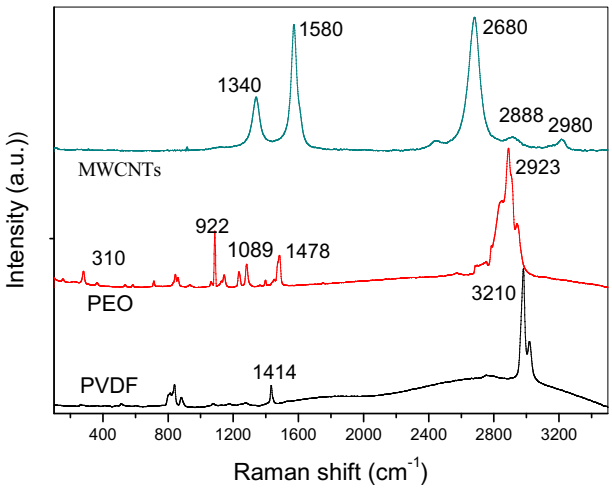

Fig. 3. Raman spectra of pure PVDF, pure PEO and MWCNTs.

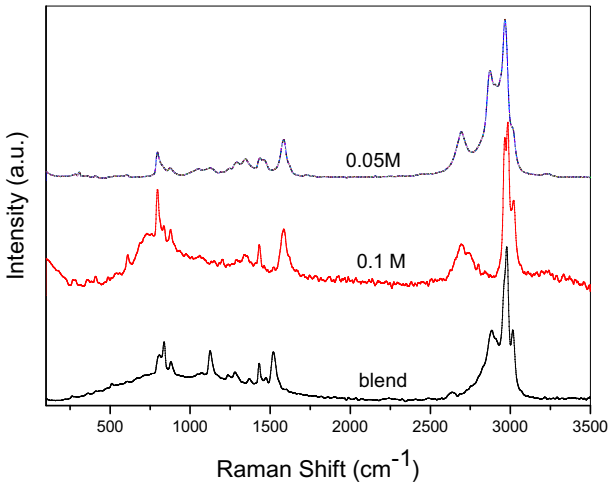

Fig. 4. Raman spectra of PEO/PVDF blend and the blend doped with 0.05 and 0.1 wt.% of MWCNTs.

For pristine PEO, the band is observed at 1486 cm^{-1} can be attributed to the in-phase bending of the CH_2 group. This mode is active in the Raman spectrum and not active in the infrared spectrum. The other band of this pair of CH_2 may not occur in the infrared spectrum but is weak in the Raman spectrum. The bands observed at 1255 and 1239 cm^{-1} are assigned to the out-of-phase twisting for the CH group, the band at 1085 cm^{-1} is corresponding to the stretching mode of the C–O group and the band at 1255 cm^{-1} may arise from disordered or amorphous portions of the polymer chain. The band at 840 cm^{-1} is due to the hydroxyl end groups (OH) in PEO [31,32].

PVDF spectra reveal that the crystal form is mainly the α-phase or form II characterized by chain conformation TGTḠ. PVDF modes are seen at 480 and 611 cm^{-1}. These modes are mainly due to CF_2 vibrations. The modes at 513 cm^{-1} attributed to CF_2 bending vibration and higher intensity band at 840 cm^{-1} due to out of phase combination of CH_2 rocking and CF_2 stretching mode. These modes are mainly as β-phase or form I of PVDF and are typical for the all-trans conformation of the PVDF chains. All-trans conformations are attributed to the strain induced by swelling in the amorphous regions. The Raman spectra of the blend doped with 0.05 wt.% and 0.1 wt.% of MWCNTS are shown in Fig. 4. The shift of the main MWCNTs bands are present in the doped samples from

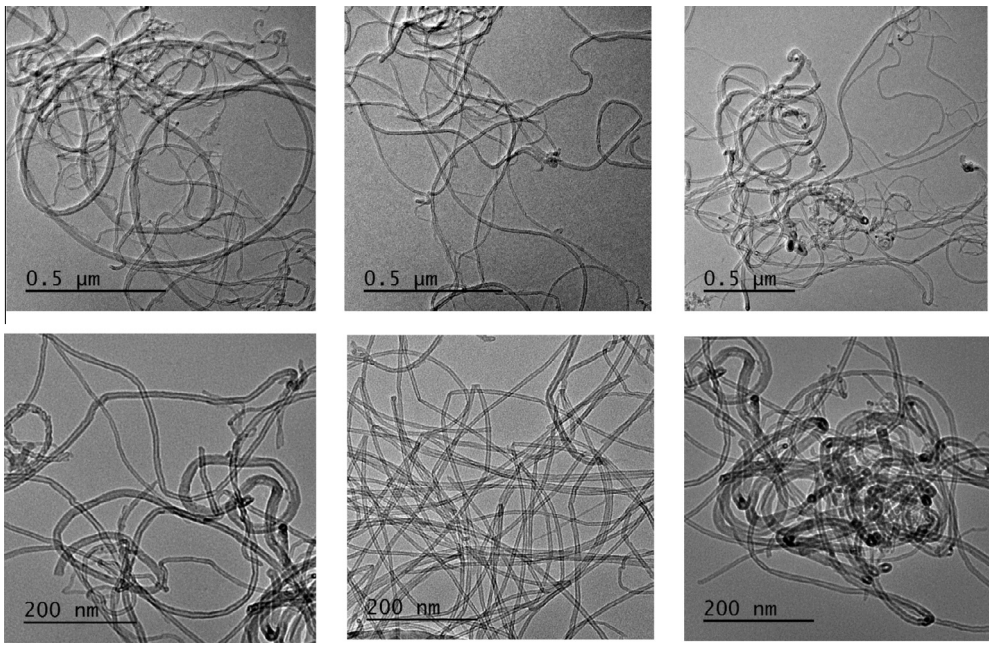

Fig. 5. TEM micrograph of SWCNT at different magnifications.

1580 cm^{-1} to 1589 cm^{-1} or the G band, from 1341 cm^{-1} to1346 cm^{-1} for the D band and from 2682 cm^{-1} to 2689 cm^{-1} for the G'' band.

3.3. TEM analysis

Fig. 5 shows the TEM micrograph of pristine MWNTs with different magnifications (0.5 μm and 200 nm). It can be seen that the surface of purified MWNTs is very clean and most of the impurity phases, such as amorphous carbon and graphitic nanoparticles are removed during the purification of MWCNTs. TEM image clearly shows MWCNTs bundles which are entangled. The diameter of the MWNTs is 8–14 nm. There are some black spots attributed to the amorphous nature of carbon. Fig. 6 shows the micrograph of MWNTs dispersion in polymer solution. MWNTs disperse well in polymeric solution, which results in uniform

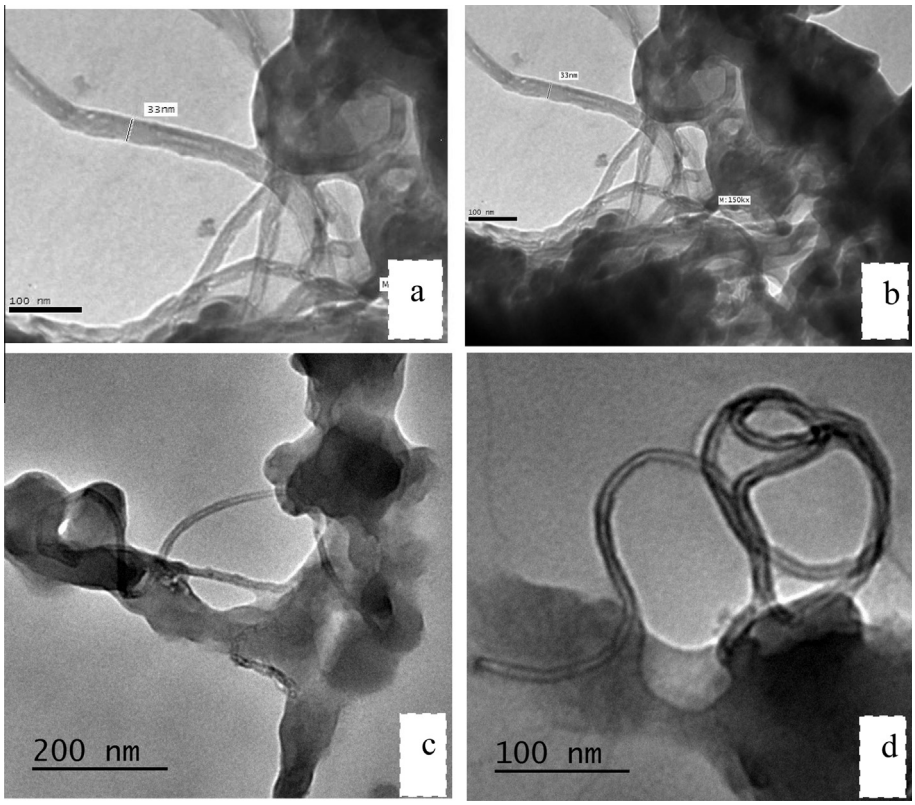

Fig. 6. TEM micrograph for PEO/PVDF blend doped with: (a, b) 0.05 wt.% and (c, d) 0.1 wt.% of MWCNTs at different magnifications.

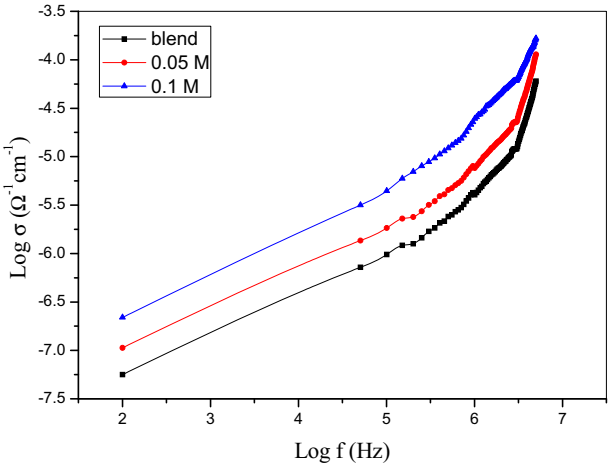

Fig. 7. The plot of Log (σ) and Log (f) of PEO/PVDF blend and the blend doped with 0.05 and 0.1 wt.% of MWCNTs.

dispersal. MWCNTs are implanted uniformly in the polymer solution and have intimate contact with these polymeric matrices. The broken ends of MWCNTs are observed revealing that the nanotubes broke apart rather than being pulled out from the fracture surface indicating the existence of strong interfacial bonding between the CNTs and the polymeric matrices. Moreover, the blend could form a dense covering layer on the images of the nanocomposites showing some defects like ragged and/or worms eaten on the tube walls. Moreover, MWCNTs are arranged in different diameters and wrapped with PEO/PVDF.

3.4. AC electrical conductivity

The AC electrical measurements (AC conductivity, dielectric permittivity ε' and dielectric loss ε'') of PEO/PVDF without and with MWCNTs were obtained at a frequency range from 42 Hz to 1 MHz and a temperature range from 303 K to 433 K. The plot of Log (σ) and Log (f) is shown in Fig. 7 for the blend and the blend with 0.05 and 0.1 wt.% of MWCNTs at room temperature. A common feature in all curves that can be seen is that the addition of MWCNTs increases and enhances the electrical conductivity of the blend. The general trend indicates that the conductivity increase attributed to charge carriers build up. The maximum conductivity has been found to be 1.64×10^{-4} S cm^{-1} at room temperature for 0.1 wt.% of MWCTs.

Fig. 8(a and b) shows the plots of Log (σ) and Log (f) at a frequency range of 42 Hz to 1 MHz with a temperature range of 303 K to 433 K. The rise of electrical conductivity with an increase of frequency is common for semiconductor and polymeric materials. This is might be due to the fact that, as the dopant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states [33]. The behavior of the curves clearly indicates an increase in the conductivity with increasing of the temperature. This is attributed to the increase in segmental

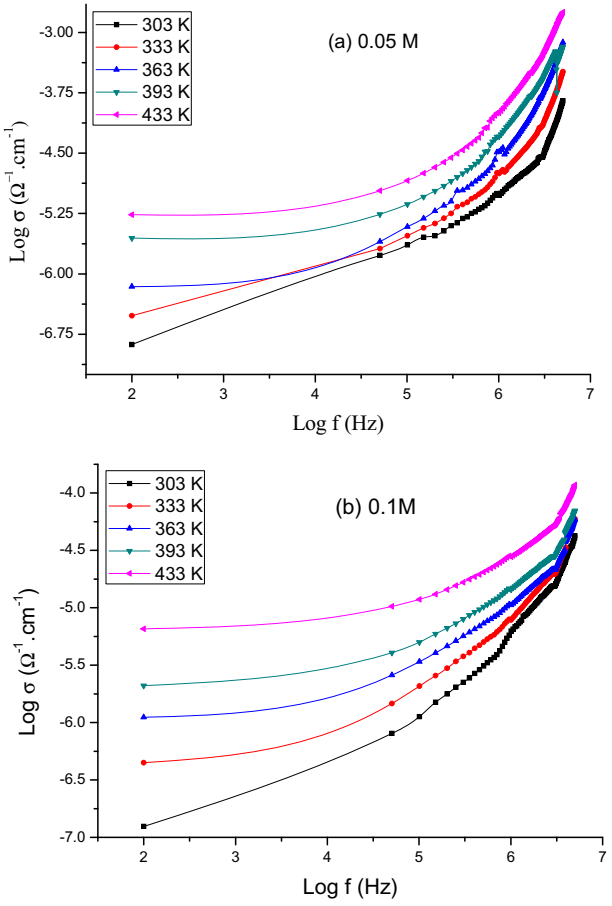

Fig. 8. Plots of Log (σ) and Log (f) at different temperatures for: (a) 0.05 wt.% and (b) 0.1 wt.% of MWCNTs.

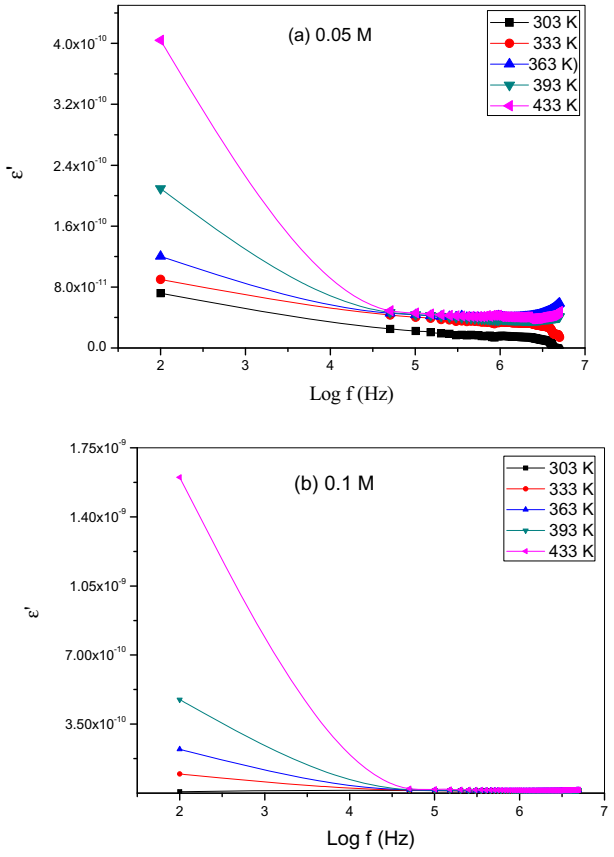

Fig. 9. Plots of dielectric constant ε' versus Log f of PEO/PVDF blend incorporated with: (a) 0.05 of MWCNTs and (b) 0.1 wt.% of MWCNTs with different temperatures.

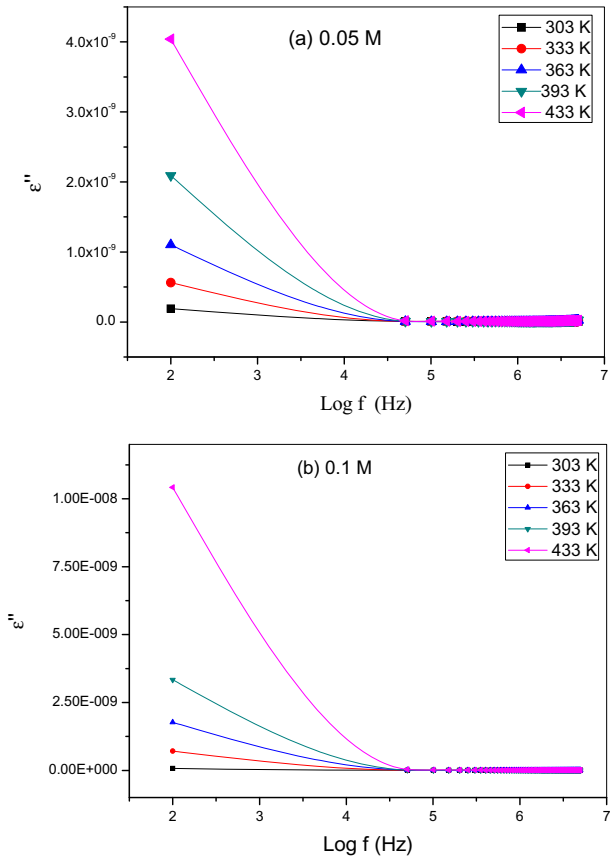

Fig. 10. Plots of dielectric loss ε'' versus Log f of PEO/PVDF blend incorporated with: (a) 0.05 of MWCNTs and (b) 0.1 wt.% of MWCNTs with different temperatures.

mobility of polymeric chains, since the specific volume of the polymer is temperature dependent, i.e., it increases as the temperature increases, the frequency and temperature dependence on conductivity is caused by the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to the states in the conduction band. A semi linear behavior is observed, means that there is no phase transition in polymeric matrices with the addition of MWCNTs in the temperature and frequencies range studies suggested that there is no dynamic conformational changes within polymeric matrices.

3.5. Dielectric analysis

The dielectric loss factors (ε' and ε'') of the prepared samples are recorded as a function of frequency. Their loss frequency spectra are investigated under a different isothermal stabilization. Figs. 9(a, b) and 10(a, b) show the plot of dielectric constant ε' and the dielectric loss ε' versus Log f of PEO/PVDF blend incorporated with 0.05 and 0.1 wt.% of MWCNTs with different temperature. From the plot it seen that both values of ε' and ε'' gradually decrease with increasing of the frequency and it reaches constant values at higher frequencies. Moreover, both values of ε' and ε'' are high at low frequencies and decreases with increase of frequencies due to polarization effects and also due to the dipoles which do not begin to follow the field variation at higher frequencies.

4. Conclusions

From FT-IR, Raman, TEM spectroscopy and AC electrical conductivity measurements, the following conclusions have been drawn. Some shifts of Raman bands occur from 1580 to 1589 cm^{-1}, from 1341 to 1346 cm^{-1} and from 2682 to 2689 cm^{-1} for G, D and G'' bands, respectively. TEM images showed that MWNTs were dispersed well in polymeric matrices. The broken ends of MWCNTs revealed that the nanotubes broke apart rather than being pulled out from the fracture surface. The PEO/PVDF blend shows some defects like ragged and/or worm eaten on the tube walls. Some black regions in TEM images were observed to be attributed to amorphous nature of carbon. The addition of MWCNTs increases and enhances the electrical conductivity of the blend attributed to charge carrier build up. The maximum conductivity has been found to be 1.64×10^{-4} S cm^{-1}at room temperature. An increase in conductivity with temperature due to the increase in segmental mobility of polymeric chains is caused by the hopping of charge carriers in the localized state and the excitation of charge carriers to the states in the conduction band. No phase transition with the addition of MWCNTs in the temperature and frequencies range studies suggested that there are no dynamic conformational changes within polymeric matrices. The values of both ε' and ε'' decreases with an increase of the frequency and it reaches constant values at higher frequencies. The values are high at low frequencies and decreases with increasing of frequencies due to polarization effects and due to the dipoles not begining to follow the field variation at higher frequencies.

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